

DEPARTMENT OF PESTICIDE REGULATION



EXECUTIVE SUMMARY
Of Report EH-91-8 Entitled
"Monitoring of the Cantara Metam-Sodium Spill"

Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulation

Background and Purpose:

On July 14, 1991, a railroad car derailed north of Dunsmuir, California, releasing 49,000 to 72,000 liters (13,000-19,000 gallons) of metam-sodium into the Sacramento River. Metam-sodium is the active ingredient in 18 pesticide products registered in California. Metam-sodium is a soil fumigant effective against weeds, soil diseases, nematodes and insects. The product that was spilled is 32.7% metam-sodium in an inert ingredient that is not of toxicological concern. The principal breakdown product, methyl isothiocyanate (MITC), causes most of the pesticidal activity. Breakdown to MITC in normal use situations occurs very rapidly, within a few hours.

Since the release of metam-sodium into the Sacramento River was caused by an accident during transport and not by its use as a pesticide, the Department of Pesticide Regulation of the California Environmental Protection Agency does not have regulatory oversight. However, because of the Department's experience in monitoring the environment for pesticide residues, Department personnel from the Environmental Monitoring and Pest Management Branch were asked to assist other state and federal agencies in documenting the changes in concentrations of MITC in the waters of Shasta Lake at two sampling sites from July 16 through July 23, 1991.

Study Methods:

Water samples were collected at two sites in Shasta Lake twice daily, in the morning and evening, for eight days. After this, other agencies continued monitoring at these sites. The northernmost site was a boat launching area at Antlers Campground located on the Sacramento River inlet to Shasta Lake, 62 kilometers (39 miles) downstream of the spill. The other was located at the Centimudi Boat Ramp approximately 800 meters (875 yards) northeast of Shasta Dam, 87 kilometers (54 miles) downstream of the spill, and 24 kilometers (15 miles) south of the sampling site at Antlers Campground.

Samples were analyzed for MITC by two laboratories: Chemistry Laboratory Services of the California Department of Food and Agriculture, and a private laboratory, the Agricultural and Priority Pollutants Laboratory (APPL), Inc. In normal use, metam-sodium would not be expected to enter surface water; therefore, neither laboratory was experienced in analyzing for either metam-sodium or its breakdown product, MITC. This meant that special care had to be taken in collecting samples and in conducting the analyses.

Major Findings

The highest MITC concentration, 5500 parts per billion (ppb), was detected at the Antlers Campground site on July 17 about 59 hours after the spill. Concentrations at this site declined to 8 ppb six days later. No MITC was detected in any sample collected from the Centimudi site. The limit of detection was 5 ppb. The results from these two sites agree with preliminary results obtained by other agencies.

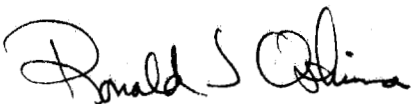
Conclusions

CDPR's monitoring alone was not enough to assess the movement, dissipation and possible effects of the metam-sodium spill. The Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency has been designated to receive all environmental monitoring data concerning the spill. Available data received by OEHHA will be reviewed. However, CDPR data provide information about levels of MITC in the water of Shasta Lake and confirm monitoring information from other agencies.

In response to the spill, OEHHA set the following interim health action levels for drinking water. These levels contain a margin of safety to protect the very young, the elderly, and other susceptible members of the population:

Metam-Sodium	Long term	0.02 milligrams/liter (mg/L) = 20 ppb
	Short term	0.35 mg/L = 350 ppb
MITC	Long term	0.05 mg/L = 50 ppb
	Short term	1.0 mg/L = 1000 ppb

Levels of MITC in the lake exceeded the short-term action level for one day and the long-term action level for three days during the eight-day sampling period. However, water from the Sacramento River from the point where the spill occurred to the area above Centimudi Boat Ramp in Shasta Lake is not used for drinking. In addition, fishing (eating fish would be another source of exposure) was not allowed in Shasta Lake from July 22 to August 5, 1991.



Ronald J. Oshima
Branch Chief

October, 1991

MONITORING OF THE CANTARA METAM-SODIUM SPILL

BY

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September 1991

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ABSTRACT

On July 14, 1991 a railroad car derailed at the Cantara Loop, north of Dunsmuir, California and spilled between 49,000 and 72,000 liters of a product containing the pesticide metam-sodium (19,000 - 27,000 kg active ingredient) into the Sacramento River. This spill posed a threat to public health and the environment. Therefore, monitoring was conducted by several agencies including the California Department of Pesticide Regulation (CDPR). Most of the pesticidal activity of metam-sodium is produced by its primary breakdown product methyl isothiocyanate (MITC).

In cooperation with the California Department of Fish and Game, the Environmental Hazards Assessment Program of CDPR collected surface water samples to help characterize the temporal distribution of MITC residues in Shasta Lake, downstream of the spill. MITC water concentrations were monitored at Antlers Campground (62 km downstream of spill) and the Centimudi boat ramp (87 km downstream of spill) between July 16 and 23, 1991.

MITC concentrations at the north end (closest to the spill) of Shasta Lake at Antlers Campground reached a maximum of 5500 ppb three days after the spill. MITC levels decreased to 8 ppb six days later. No MITC was detected at the Centimudi Boat Ramp located at the southern end of Shasta Lake (detection limit 5 ppb).

This monitoring alone is not enough to assess the movement, dissipation and possible effects of the metam-sodium spill. When the data from all monitoring groups are available, such an assessment will be possible.

ACKNOWLEDGEMENTS

The authors wish to thank the hard-working members of the Environmental Hazards Assessment Program's field group and the the California Department of Food and Agriculture Chemistry Lab's environmental monitoring section. Thanks also to Linda Heath for preparing the graphics and to the owners of the Antlers Campground.

DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as an actual or implied endorsement of those products.

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INTRODUCTION

On July 14, 1991 a Southern Pacific railroad car carrying Alco Metam Sodium™ derailed at the Cantara Loop, north of Dunsmuir, California and spilled between 49,000 and 72,000 liters (13,000 - 19,000 gal) of the product into the Sacramento River. The spilled material degraded to several toxic and volatile chemicals which could pose a threat to public health and the environment. Of particular concern were the people living in small communities adjacent to this part of the river, the aquatic organisms in the river, and Shasta Lake, downstream of the spill which is a major recreation area and drinking water reservoir. For these and other reasons monitoring was conducted by several agencies, including the California Department of Pesticide Regulation (CDPR).

Alco Metam Sodium™, formulated by the Amvac Chemical Corporation, contains 32.7% metam-sodium (by weight) as the active ingredient. Assuming 49,000 - 72,000 L of the product were released into the river, 19,000 - 27,000 kg (42,000 - 60,000 lbs) of active ingredient would have been spilled into the river. This chemical is used agriculturally as a fungicide, herbicide, insecticide, nematocide and soil fumigant. Most of its pesticidal action is produced by its primary breakdown product, methyl isothiocyanate (MITC). Breakdown to MITC normally occurs very rapidly, within a few hours. Other chemicals are also produced from the breakdown of metam-sodium, including hydrogen sulfide, carbon disulfide, and methylamine. See Appendix 1 for references and more details about the environmental fate of metam-sodium.

Monitoring by the CDPR was conducted by the Environmental Hazards Assessment Program (EHAP) in cooperation with the California Department of Fish and Game. Water was sampled over time at two locations on Shasta Lake (Figure 1). The purpose of the monitoring by the EHAP was to characterize the temporal distribution of MITC in Shasta Lake.

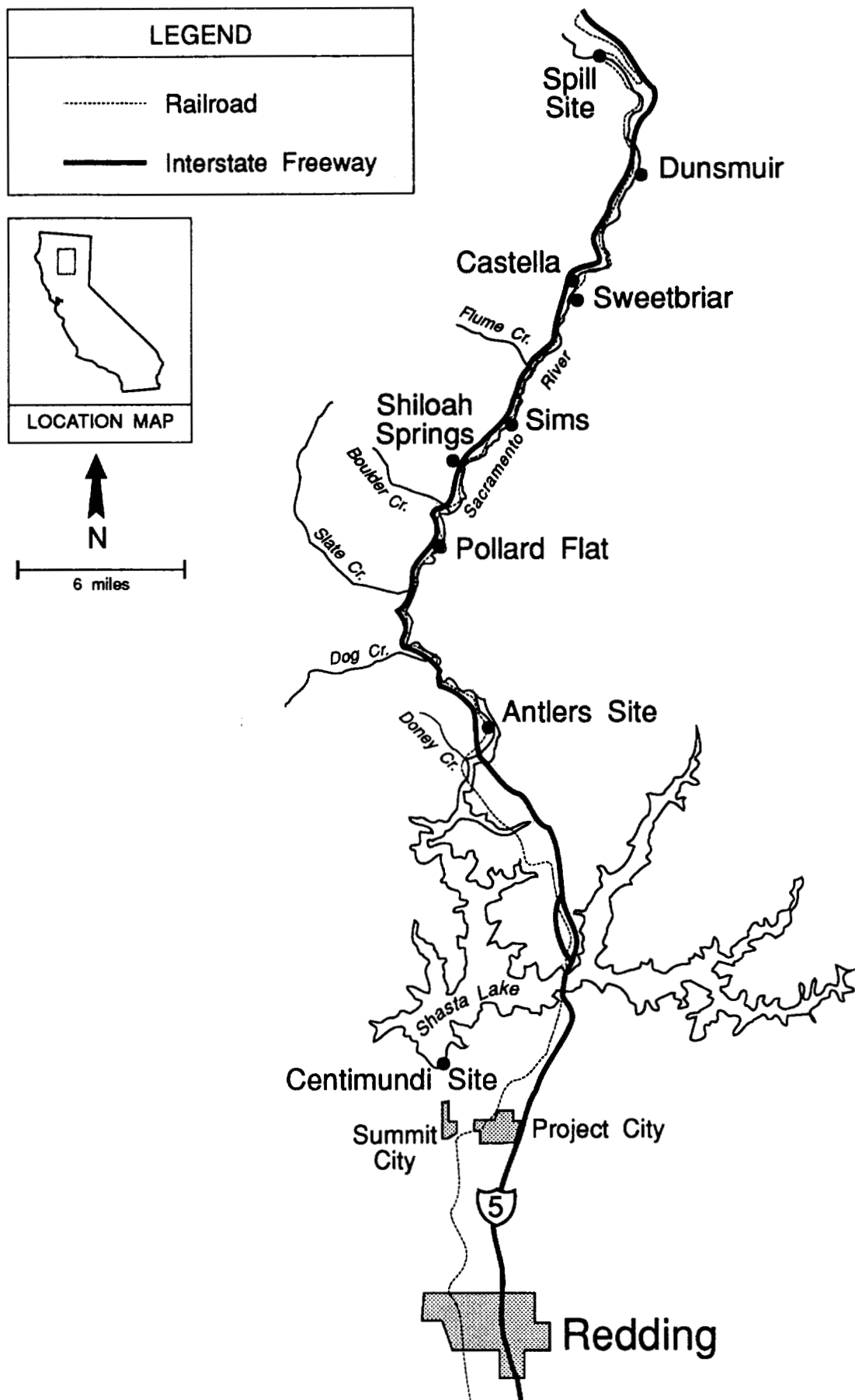


Figure 1. Location of metam-sodium spill and downstream areas

MATERIALS AND METHODS

Sample Collection

Water samples were collected from two sites in Shasta Lake (Figure 1) twice daily. Site 1 was a boat launching area at Antlers Campground located on the Sacramento River inlet to Shasta Lake, 62 km (39 mi, by river) downstream of the spill site. It is a narrow channel at the north end of the lake which expands into a wide bend to the south. Site 2 was located at the Centimudi boat ramp which is located approximately 800 m northeast of Shasta Dam, 87 km (54 mi, by river) downstream of the spill site. Sampling was initiated on July 16, 1991 at 9:05 in the morning. Samples continued to be collected twice a day, once in the morning and once in the evening. The last set of samples was collected the morning of July 23.

One-liter amber glass bottles and 40 mL glass vials were submerged approximately two meters from the lake edge and 50 cm below the water surface to collect the samples. The containers were filled to capacity and then capped under water with teflon-lined lids. This procedure reduced the possibility of trapping air inside the containers. Containers were checked to determine if air was trapped inside by inverting the sample. Each sample was accompanied by a chain of custody which documented its history. The pH and water temperature of each sample were also measured.

The samples were placed on wet ice (4°C) immediately after sample collection. Samples were kept under refrigeration during transport until delivery to the CDPR West Sacramento facility. Samples were checked in at the West Sacramento facility and then delivered to the laboratory for analysis.

Chemical Analysis and Quality Control

Samples were analyzed for MITC by two laboratories, the California Department of Food and Agriculture, Chemistry Laboratory Services Branch (CDFA) and the Agricultural and Priority Pollutants Laboratory, Inc. (APPL). The primary method, by CDFA, consisted of direct sample injection into a high pressure liquid chromatograph with a post-column reactor and a fluorescence detector. Samples that were positive using this method were confirmed by the CDFA laboratory by extracting the water samples with a minimum amount of carbon disulfide and injecting the extract into a gas chromatograph equipped with a nitrogen-phosphorous detector. APPL confirmed all samples using a purge and trap apparatus equipped with photoionization and flame ionization detectors. Details of the MITC analytical methods are given in Appendix 2.

Analysis for other chemicals was attempted. The CDFA laboratory analyzed for a combination of metam-sodium and carbon disulfide. Their method incorporated a step to convert metam-sodium to carbon disulfide and analyzing for total carbon disulfide. No distinction was made between true carbon disulfide present in the sample and carbon disulfide that was present as the result of metam-sodium conversion.

Several measures were taken to insure valid results were obtained. To protect against sample tampering, each bottle was accompanied with a chain of custody form which was signed by every individual who handled the sample. Laboratory results and field notes were also written on the chain of custody forms. To check for sample contamination, blank samples were created in the field and in the laboratory. Field blanks were created by pouring distilled water into sample bottles at the same time and place as the actual samples. Additional blanks were created in the laboratory. For a qualitative check, all positive samples were confirmed using the solvent extraction method described above; this method was not used to quantitate. To check for quantitation, spiked samples (known amount of MITC added to a sample) were submitted to the laboratory disguised as real

samples. In addition, the purge and trap method described above was used to quantitate concentrations. To check for possible dissipation during storage, a storage stability test was conducted. This test consisted of storing a set of spiked samples under the same conditions as real samples and analyzing them over a period of six days.

RESULTS AND DISCUSSION

Results of the water monitoring are shown in Tables 1 and 2 and Figure 2. The highest MITC concentration, 5500 ppb, was detected at the Antlers Campground site on July 17. Concentrations declined from the peak, to 8 ppb six days later. No MITC was detected in any sample collected from the Centimudi site (detection limit 5 ppb). These results agree with preliminary results obtained by other agencies.

Results of the quality control analyses were good. None of the blank samples were positive and there was good agreement between laboratories. Recoveries of the two blind spike samples were both 100%. The storage stability test indicated that no dissipation occurred during the time between sampling and analysis. The quality control raw data are shown in Appendix 3.

Thirteen samples that were positive for MITC were also analyzed for metam-sodium/carbon disulfide, as described earlier. Only one which corresponded to the sample that contained 5500 ppb of MITC was able to be quantified at 1240 ppb of carbon disulfide. If all of the carbon disulfide detected was converted metam-sodium, then the original metam-sodium concentration would have been 2100 ppb (adjusted for stoichiometric change in molecular weight). The CDFA laboratory also attempted to analyze for hydrogen sulfide, but could not develop an adequate method.

This monitoring alone is not enough to assess the movement, dissipation and possible effects of the metam-sodium spill. When the data from all monitoring groups are available, such an assessment will be possible.

Table 1. Results of the Cantara metam-sodium spill water monitoring at Antlers Campground, Shasta Lake.

Date	Time	Methyl Isothiocyanate (ppb)		pH	Temperature (°C)
		CDFA	APPL		
7/16/91	0905	None Detected ^a		7.2	21.1
	1830	None Detected		7.6	21.8
7/17/91	0825	5500	5800	7.8	19.8
	1805	1580	1600	7.9	25.4
7/18/91	0850	454	474	7.2	20.3
	1815	242	170	7.4	25.4
7/19/91	0645	134	broken	7.4	21.2
	1830	85	70	7.4	25.6
7/20/91	0700	61	54	7.4	21.6
	1800	44	36	7.9	25.4
7/21/91	0645	35	27	7.5	21.7
	1740	22	20	7.6	26.4
7/22/91	0700	20	16	7.5	22.3
	1830	12	12	7.6	26.1
7/23/91	0730	8.0	8.3	7.4	22.1

a - CDFA detection limit = 5.0 ppb, APPL detection limit = 2.0 ppb

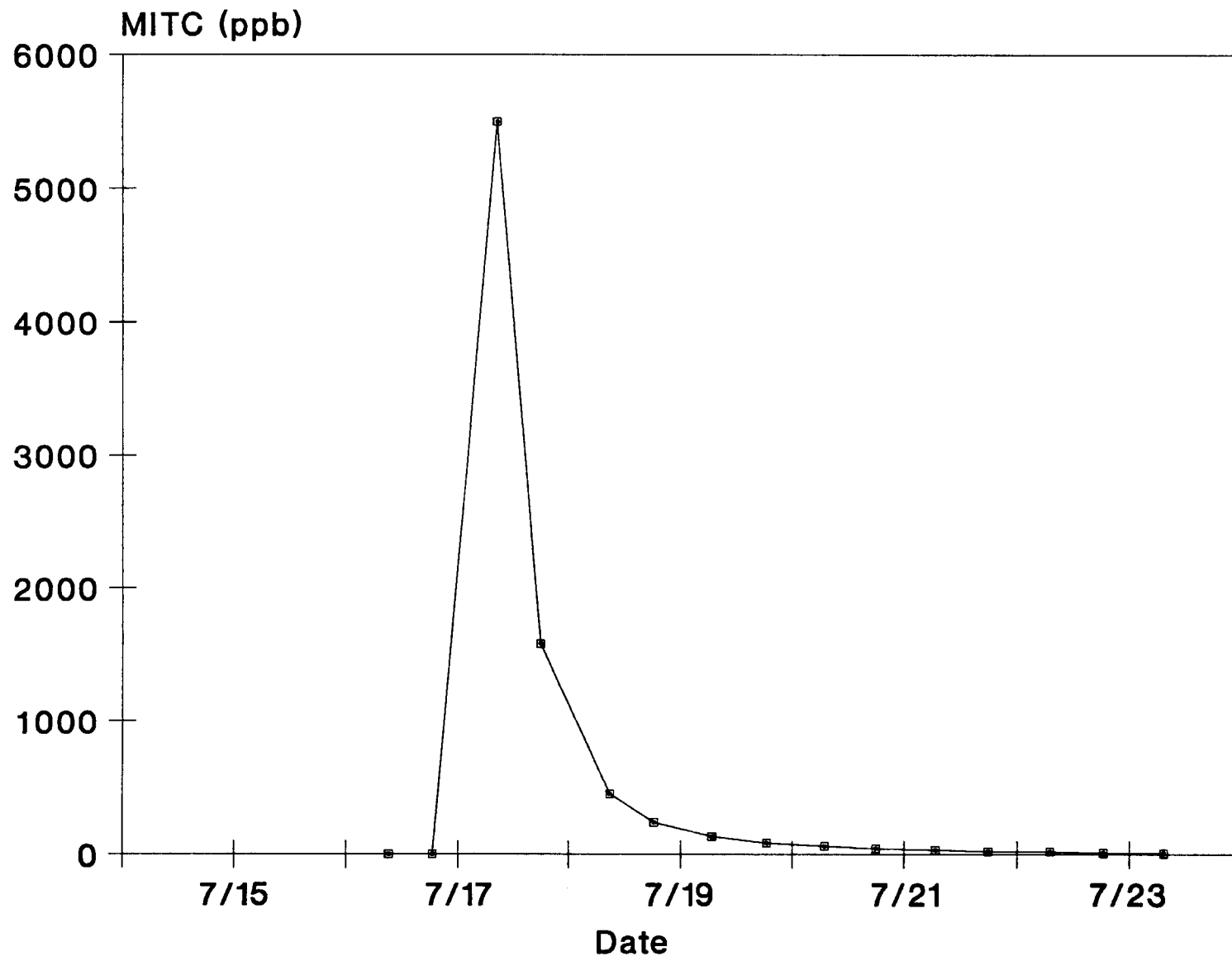
Table 2. Results of the Cantara metam-sodium spill water monitoring at the Centimudi Boat Ramp, Shasta Lake.

Date	Time	Methyl Isothiocyanate (ppb)		pH	Temperature (°C)
		CDFA	APPL		
7/16/91	1010	None Detected ^a		7.6	25.7
	1925	None Detected		7.8	25.8
7/17/91	0945	None Detected ^b		8.0	25.6
	1920	None Detected ^b		8.2	28.0
7/18/91	1010	None Detected		7.9	26.3
	1945	None Detected		7.8	27.7
7/19/91	0830	None Detected ^b		7.6	26.4
	1945	None Detected		7.8	26.5
7/20/91	0815	None Detected		7.8	25.8
	1915	None Detected		7.6	25.9
7/21/91	0800	None Detected		7.4	25.3
	1840	None Detected		7.8	28.9
7/22/91	0800	None Detected		7.9	26.9

a - CDFA detection limit = 5.0 ppb, APPL detection limit = 2.0 ppb

b - APPL sample broken, no analysis

Figure 2. MITC at Antlers Campground



MONITORING BY OTHER AGENCIES

The CDPR monitoring program was very minimal. Extensive monitoring has been and continues to be conducted by other agencies, particularly by the Regional Water Quality Control Board. In addition, the Cal EPA Office of Environmental Health Hazard Assessment is acting as a central repository for all monitoring data. Listed below are the agencies conducting monitoring; the list may not be complete.

U.S. Bureau of Reclamation: water monitoring

Cal EPA - Regional Water Quality Control Board, Central Valley Region: water, soil, and sediment monitoring

Cal EPA - Air Resources Board: air monitoring

Cal EPA - State Water Resources Control Board: air monitoring

Cal EPA - Department of Toxic Substances Control: water, soil, and sediment monitoring

California Department of Fish and Game: water, sediment, and biota monitoring

California Occupational Safety and Health: air monitoring

California Department of Health Services: water monitoring

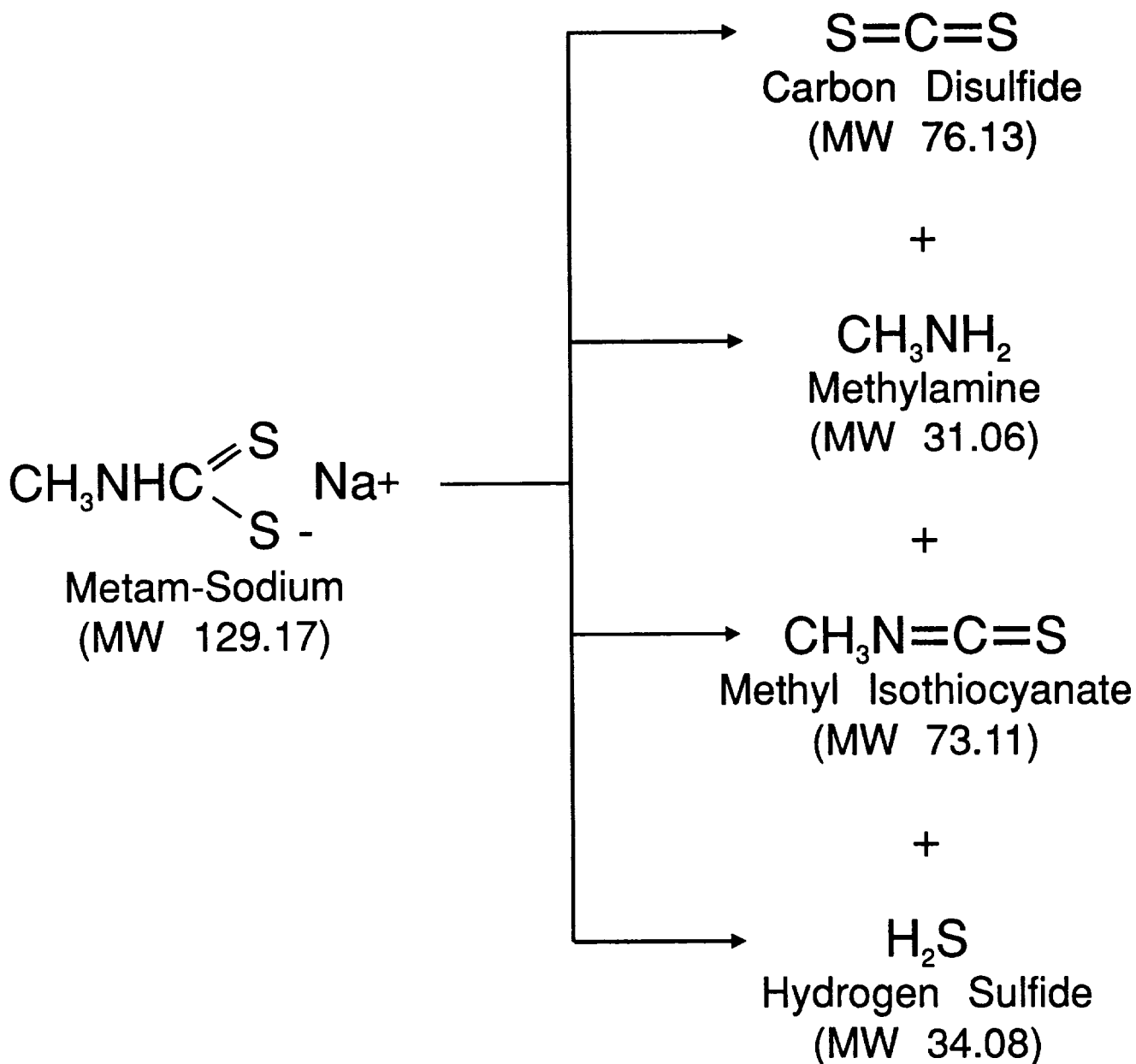
Shasta County Department of Environmental Health: groundwater monitoring (public and private drinking water wells)

Southern Pacific - Terra and OHM (under contract): water, air, soil, and sediment monitoring

In addition, the California Department of Fish and Game is conducting biological surveys for impacts to fish, wildlife and vegetation.

Appendix 1 - Environmental Fate of Metam-Sodium

Degradation Pathways for Metam-Sodium



Molecular weight is shown in parentheses

Memorandum

To : Don Weaver
Sr. Environmental Research Scientist
Environmental Hazards Assessment Program

Date : November 20, 1990

Place : Sacramento

From : Department of Food and Agriculture Chris Collison, Assoc. Env. Research Scientist
Environmental Hazards Assessment Program

Subject : LITERATURE REVIEW OF THE ENVIRONMENTAL FATE OF METAM-SODIUM (VAPAM®)

This review was based on data from the CDFA pesticide registration packages cited as Stauffer Chemical Company and ICI Americas, Inc., and from open literature articles.

Metam-sodium (sodium methyldithiocarbamate) is the active ingredient in Vapam®, a broad-spectrum soil fumigant produced by Stauffer Chemical Company. It is commonly applied as a preplant fumigant incorporated into the irrigation system.

Conversion In Soil

Metam-sodium degrades rapidly to methyl isothiocyanate (MITC) when in contact with moist soil. Smelt and Leistra (1974) found that the conversion of metam-sodium to MITC (>90%) took only a few hours. In experiments using spiked moist soil in glass septum flasks incubated at 12°C, conversion was complete in 3 hours in loamy soils and in 6 hours in a humic sandy soil. At 21°C in the sandy soil, a period of 3-4 hours was sufficient for conversion to MITC.

The decomposition rate of MITC in moist soil was also investigated (Smelt and Leistra, 1974). Depending on the soil type, half-lives for MITC were in the range of 8-14 days. The most rapid decomposition occurred in heavy, loamy soils at higher temperatures. Smelt et al. (1989) also investigated decomposition rates of MITC in "problem" soils (those demonstrating inadequate pest control by fumigation with metam-sodium). MITC in amounts ranging from 1.5 to 2.0 mg (equivalent to 150 kg/ha) was added to glass flasks partially filled with moist soil and incubated in the dark at 15°C. A comparison of the decomposition patterns of MITC in previously treated and untreated soils showed that, in general, MITC degraded much faster in the previously treated soils. This suggested that repeated applications of metam-sodium induced microbial adaptation resulting in enhanced biotransformation of MITC. In this study, MITC half-lives ranged from 0.5 to 50 days. The study results also indicated that the decomposition rate of MITC greatly depends on the initial content of the fumigant.

Soil Mobility

In two field studies conducted "under normal agricultural conditions" in Mississippi and California by ICI Americas, Inc. (1989), MITC was found no deeper than 9 inches in soil and undetected at any depth 13 days after application. Vapam was applied to bare fallow soil at a rate of 100 gallons of formulated material (32.7% AI) per acre by chemigation with an overhead sprinkler. The respective zero-time MITC residues were 18 and 42 ppm in the upper 6 inches of soil in Mississippi and California. Half-lives were 13 and 26 hours in loam soil near Visalia, California and loam/silt-loam soil near Leland, Mississippi respectively. Four days post application, maximum residues of the degradation product 1,3-dimethylurea were from 0.13 to 0.51 ppm.

Leaching experiments were performed by Stauffer Chemical Company (1985a) using 32-37 cm long glass and steel columns hand packed with soil. A radiolabeled ^{14}C metam-sodium solution was used to spike the columns at concentrations equivalent to 1 quart/100 sq ft and, at the highest application rate recommended, 2 quarts/100 sq ft. Four soil types ranging from sand to loamy sand to sandy clay were tested. In each case, about 60% of the applied ^{14}C leached from the columns after 48 mL of water were poured on the soil (equivalent to 20 inches X the cross sectional area of the columns). About 90% of the leached ^{14}C was identified as MITC. Results indicated that the bulk of the soluble ^{14}C leached out of the soil soon after the volume of water necessary for soil saturation was added. Between 11 and 14% of the applied ^{14}C remained bound to the soil and 23 to 30% was assumed to have been lost as volatile degradation products, mainly MITC.

Volatile Emissions

Emissions of MITC from greenhouse soil were studied by Leistra and Crum, (1990). Concentrations of MITC in treated soil were measured and the data was used in a computer model to simulate emissions from the soil. The experimental fumigation was conducted in a greenhouse with wetted, sandy soil cultivated to a depth of 0.25 m. Two hundred and forty liters of the trade product (510 g metam-sodium per liter), which corresponds to 1950 L/ha of the trade product, was applied with a small self-propelled shank injector to a depth of 0.05-0.10 m. A 30 μm thick low density polyethene film was used to completely cover the soil after application and was left on the soil surface for 7 days. Before removal of the cover, the cumulative emission of MITC from the greenhouse soil was computed to be about 45% of the applied dosage. At day 14, seven days after removal of the cover, the total cumulative emission was 50% of the applied dosage.

The highest rate of emission from the film-covered soil occurred on the first day after application. Concentrations in greenhouse air were computed to be around 50 mg/m on the first day and exceeded 10 mg/m during the first 4 days after injection. When the model was modified to exclude the factor of a film cover, the computed MITC emission rate one day after application was 2.5 times greater than the rate with a film cover. The cumulative emission after 14 days without a film cover was computed to be 64% of the applied dosage. The vapor pressure of MITC is 2.7 kPa at 20°C (Hartly and Kidd, 1983).

The emission model was further modified to simulate the homogeneous incorporation of metam-sodium into the soil to a depth of 0.24 m after a surface application. The results indicated a somewhat lower emission rate in the first 3-4 days. After about 4 days, the emission rate was similar to that for injection. At the end of the 14 day period, the computed cumulative emission corresponded to 38% of the applied dosage. Without a film cover, the emission was 49% of the equivalent dosage.

Hydrolysis

Half-lives for metam-sodium at 20°C in dilute solutions at pH 5, 7, and 9 were 23, 180, and 46 hours respectively. The major products of hydrolytic degradation at pH 5 were methylamine, MITC, and carbon disulfide. Minor hydrolytic degradation products included elemental sulfur and 1,3-dimethylthiourea (Stauffer Chemical Company, 1985b).

Photolysis

The major products arising from photolysis of metam-sodium in aqueous solution (120 ppm) at 25°C and pH 7 were MITC, N-methylthioformamide, methylamine, and elemental sulfur. Minor photolytic degradation products included N-methylformamide, carbon disulfide, carbon oxide sulfide, and hydrogen sulfide. Under these conditions, the half-life for metam-sodium was 1.6 hours (Stauffer Chemical Company, 1985b)

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Don Weaver
November 20, 1990
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Stauffer Chemical Company. 1985b. Hydrolysis and photolysis of metam-sodium. CDFA Doc. 50150-006.

cc: Ronald J. Oshima
John Sanders
Randy Segawa
Kean Goh

Appendix 2 - Chemical Analysis Methods

CALIFORNIA DEPT. OF FOOD & AGRIC.
ENVIRONMENTAL MONITORING SECTION
CHEMISTRY LABORATORY SERVICES
3292 Meadowview Road
Sacramento, CA 95832
(916)+427-4408

Original Date: July 17, 1991
Supersedes: New
Current Date: August 14, 1991
Method #: ??

METHYL ISOTHIOCYANATE IN RIVER WATER BY HPLC AND GC

SCOPE:

This method is for the determination of methyl isothiocyanate (MITC) in river water. Its sensitivity is 5 ppb.

PRINCIPLE:

HPLC method:

The water samples are directly injected to HPLC, separated on a reverse phase octadecyl bonded column. The eluant is derivatized with OPA by post column reaction and detected with a fluorescence detector (Excitation-340 nm, Emission-450 nm).

GC method:

MITC in water is extracted with a minimum amount of carbon disulfide. The extracts are analyzed by GC with a nitrogen specific detector.

REAGENTS AND EQUIPMENT:

Distilled water, HPLC grade

Acetonitrile, HPLC grade

Carbon disulfide, residue grade

Disposable filters 0.2 micron (Nylon Acrodisc).

HPLC - Hewlett Packard HP 1090 Liquid Chromatograph controlled by HP 79994A
HPLC ChemStation™

Fluorescence Detector - Hewlett Packard HP 1046A

Post Column derivatization system - Pickering Laboratory CRX 390 high temperature reaction control device, two Milton Roy miniPumps™ with pressure readout devices and an ambient temperature reaction coil.

Reagent A, 0.2% NaOH/H₂O

Reagent B, Dissolve 0.5 gram of o-Phthalaldehyde in 10 mL of methanol, add 1 mL 2-mercaptoethanol, then add 50 mL of pH 10.4 buffer (1 M of Potassium borate), and dilute to 1 L with distilled water.

ANALYSIS:

PRIMARY ANALYSIS (HPLC)

Sample Preparation:

1. Filter the water sample, using a 10 mL hypodermic syringe, through a 0.2 micron nylon Acrodisc filter into an autosampler vial. Seal the top with a crimp top cap.

PRIMARY ANALYSIS (HPLC)

Sample Preparation: continued.

2. The content of the autosampler vials is ready for HPLC analysis.

Instrument Conditions:

Column: Beckman Ultrasphere ODS C-18, 5 micron 4.6 mm X 25 cm.

Sample Loop: 250 microliter

Sample injection: 250 microliter (same volume of standard and sample injected)

Mobile Phase: Gradient

Time (minutes)	% Water	% Acetonitrile
0.0	90	10
1.0	90	10
6.0	30	70
10.0	30	70
13.0	90	10

Retention time of MITC: 9.624 min (SD=0.018min, n=20)

Flow: 1.0 ml/min

Post Column System:

Flow: Reagent A 0.2 ml/min
Reagent B 0.2 ml/min

Detector: Fluorescence Excitation - 340 nm Emission - 450 nm

METHOD VALIDATION:

This method for water analysis does not require solvent extraction. Samples are directly injected to the HPLC system. Thus, the method recovery is at about 100% level. The variation in recoveries is mainly due to the performance of the instrument.

Spike Level ppb	MITC % Recovery	SD	Percent Variation	n
5	92.6	0.32	6.5	5
20	105.2	0.74	3.7	5
100	102.2	1.5	1.5	5
500	97.5	4.0	0.8	5
1000	102.2	5.0	0.5	5

CALCULATIONS:

$$\text{PPB} = \frac{(\text{peak area sample})(\text{concentration of std ng/ul})(1000 \text{ ul/ml})}{(\text{peak area std})}$$

CONFIRMATION ANALYSIS (GC)**Sample preparation:**

1. Remove sample from refrigerated storage.
2. Shake sample and weigh out 500 g by difference and transfer this aliquot to a 1 L separatory funnel.
3. Extract sample by adding 10 mL of carbon disulfide and shake vigorously for 1 minute.
4. Allow the layers to separate and drain the lower layer into a 25 mL test tube.
5. Repeat the extraction one more time using 10 mL carbon disulfide. Combine the extracts.
6. Add approximately 1 g sodium sulfate and shake to remove water.
7. The extract is ready for GC analysis.

Instrument conditions:

Varian 3700 GC with NPD

Column: HP-FFAP (cross-linked polyethylene glycol-IPA modified) 10 m x 0.53 mm x 1.0 um

Column temperature: 50°C/1 minute, program at 10°C/minute to 110°C

Retention time: 2.60 min

Injector temperature: 200°C

Detector base temperature: 220°C

DISCUSSION:

MITC is very volatile. Rotary vacuum evaporation and open beaker evaporation yields no recovery. Kuderna-Danish solvent evaporation which is very tedious can produce approximately 60% recovery. Thus, to avoid these problems we chose to use a minimum amount of solvent for extraction and not to concentrate the extract. The average recovery of this solvent extraction method is 60-70%.

The HPLC method is superior to the GC method. It requires no solvent extraction. The recoveries are approximately 100%.

REFERENCE:

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REVIEWED BY: Catherine Cooper

Sybil Robinson (acting)
TITLE: Supervising Chemist

APPROVED BY: Terry Jackson

Robert Knight for Terry Jackson
TITLE: Quality Assurance Officer

APPROVED BY: Mark Lee

Larry Chambers (for Mark Lee)
TITLE: Research Agricultural Chemist

MITC in water by Modified EPA Method 602

Equipment:

- 1) Gas chromatograph: HP Model 5890
- 2) Detector: OI Tandem PID/FID
- 3) Column: 30m DB624
Temperature program: 50°C for 3 minutes; 8°C/Min. to 200°C.
Hold 0.25 min. Run time = 22 minutes RT MITC = 7.1 min.
- 4) Purge and Trap: Tekmar Model 4000
Trap: 1 cm 3%SP-2100, 23 cm Tenax. Supelco #2-0295M
Purge Time: 11 min. at <30°C
Desorb Time: 3 min. at 180°C
Brake Time: 6 min. at 225°C
- 5) Autosampler: Dynatech Precision Sampling PTA30-WS

Procedure:

- 1) Prepare a calibration curve from a 1000 ppm MITC stock solution in methanol. A five point curve is run at 5, 10, 25, 50 and 100 µg/L. Prepare spikes at 10-25 µg/L.
- 2) Load autosampler with standards and samples in 40 ml VOA vials in the following order: Blank, calibration curve, spikes, 10 samples, midpoint standard (25 µg/L), spikes, 10 samples, blank, midpoint standard, etc.
- 3) Set the autosampler to purge 10 ml aliquots in the water mode using internal standard addition. The internal standard solution is 100 ppm of Volatiles Internal Standards Mix 502 (Supelco)
- 4) The Turbochrom III calculates spike and sample amounts off the calibration curve. Peak area and internal standard calculation is used. Linearity must be ≥ 0.997 . A new calibration curve is run whenever the midpoint standard has a linearity below 0.997. Samples containing MITC > 100 µg/L are diluted and rerun.
- 5) µg/L MITC in chromatography report times the dilution is µg/L MITC in sample.

Appendix 3 - Quality Control Data

Comparison of CDFA and APPL Results MITC Water Concentrations

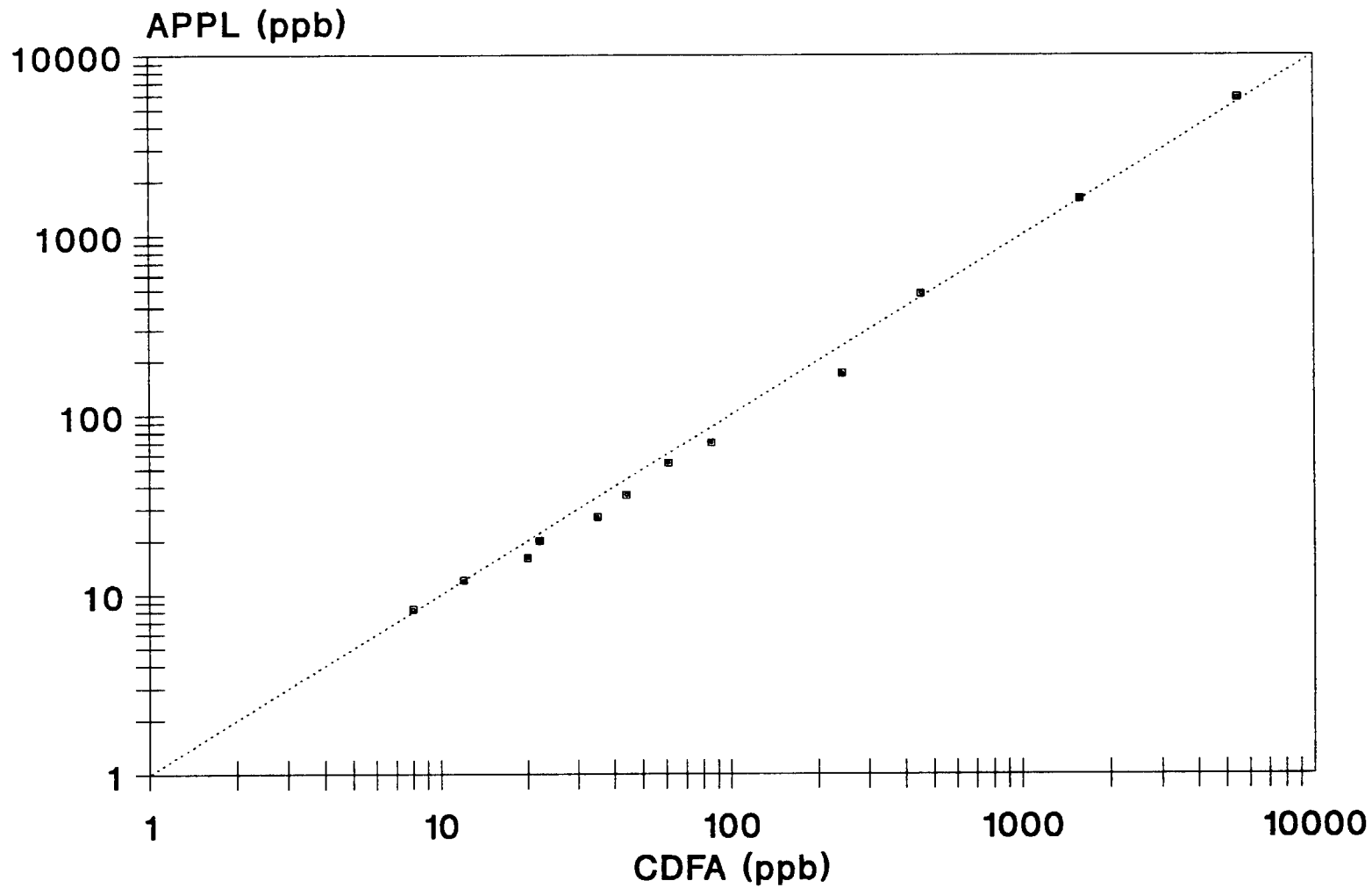


Table 3-I. Method validation data (% recoveries) for the Metam Sodium Study.

Study: X56
 Analyte: MITC
 MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Paul Lee
 Method: GC/NPD

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
134	3.81	5.0	76			
134	3.33	5.0	67			
134	3.33	5.0	67	70	5.2	7.4
136	7.13	10.0	71			
136	7.56	10.0	76			
136	7.56	10.0	76	74	2.9	3.9
135	38.51	50.0	77			
135	41.84	50.0	83			
135	43.95	50.0	87	82	5.0	6.1
OVERALL:				76	6.7	8.8

Table 3-II. Method validation data (% recoveries) for the Metam Sodium Study.

Study: X56
 Analyte: MITC
 MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Paul Lee
 Method: HPLC/ post column/ fluorescence

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
390	4.4	5.0	88			
390	5.0	5.0	100			
390	5.0	5.0	100			
390	4.4	5.0	88			
390	4.5	5.0	90	93	6.3	6.7
389	22	20	110			
389	21	20	105			
389	21	20	105			
389	20	20	100			
389	21	20	105	105	3.54	3.37
388	100	100	100			
388	101	100	101			
388	104	100	104			
388	103	100	103			
388	102	100	102	102	1.58	1.55
387	493.3	500	98.6			
387	485.6	500	97.1			
387	486.2	500	97.2			
387	482.9	500	96.6			
387	489.5	500	97.9	97	0.8	0.8
386	1028	1000	102.8			
386	1027	1000	102.7			
386	1023	1000	102.3			
386	1015	1000	101.5			
386	1020	1000	102.0	102	0.53	0.52
OVERALL:				100	5.22	5.22

Table 3-III. Continuing quality control data for the Metam Sodium Study.

Study: X56
 Analyte: MITC

MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Paul Lee
 Method: GC/NPD

Extraction Set No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
31, 43, 49, 55	385	15	20	75			
7	383	7.27	10	73			
OVERALL:					74	1.4	1.9

Table 3-IV. Continuing quality control data for the Metam Sodium Study.

Study: X56
 Analyte: MITC

MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Paul Lee
 Method: HPLC/ post column/ fluorescence

Extraction Set No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
25	380	1000	1000	100			
1, 13	378	1012	1000	101			
221, 233, 239, 227, 245, 197, 226, 202, 232, 238	377	98.3	100	98			
137, 167, 140, 142, 209, 258, 364, 370, 155, 382, 394, 161, 127	375	100	100	100			
251, 376, 413, 407, 501, 455, 388, 479, 482, 504, 458, 391, 381, 256, 418, 412	367	97.2	100	97			
417, 425, 431, 437, 424, 507, 430, 436, 442	373	99.3	100	99			
401, 406, 449, 454, 508	370	97.20	100	97			
OVERALL:					99	1.6	1.6

Table 3-V. Storage dissipation data for the Metam Sodium Study (room temperature, pH 7.5).

Study: X56
 Analyte: MITC
 MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Jean Hsu
 Method: GC/NPD

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
202	0	7/19/91	7/19/91	156	200	78			
203	0	7/19/91	7/19/91	154	200	77	78	0.71	0.91
211	1	7/20/91	7/20/91	159	200	79			
212	1	7/20/91	7/20/91	148	200	74	77	3.5	4.6
220	2	7/21/91	7/21/91	152	200	76			
222	2	7/21/91	7/21/91	149	200	72	74	2.8	3.8
230	3	7/22/91	7/22/91	156	200	76			
231	3	7/22/91	7/22/91	138*	200	69	73	4.9	6.8
267	4	7/23/91	7/23/91	145	200	73			
268	4	7/23/91	7/23/91	152	200	76	75	2.1	2.8
276	5	7/24/91	7/24/91	131	200	66			
277	5	7/24/91	7/24/91	131	200	66	66	0.0	0.0
303	6	7/25/91	7/25/91	134	200	67			
304	6	7/25/91	7/25/91	128	200	64	66	2.1	3.2

OVERALL: 72 5.0 7.0

* Low recovery due to leak during extraction.

Table 3-VI. Storage dissipation data for the Metam Sodium Study (refrigerated, pH 7.5).

Study: X56
 Analyte: MITC
 MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Jean Hsu
 Method: GC/NPD

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
204	0	7/19/91	7/19/91	151	200	76			
205	0	7/19/91	7/19/91	156	200	78	77	1.41	1.84
213	1	7/20/91	7/20/91	145	200	72			
214	1	7/20/91	7/20/91	146	200	73	73	0.71	0.98
223	2	7/21/91	7/21/91	124*	200	62			
224	2	7/21/91	7/21/91	141	200	71	67	6.4	9.6
232	3	7/22/91	7/22/91	156	200	76			
233	3	7/22/91	7/22/91	156	200	76	76	0.0	0.0
269	4	7/23/91	7/23/91	141	200	71			
270	4	7/23/91	7/23/91	145	200	72	72	0.71	0.99
278	5	7/24/91	7/24/91	145	200	72			
279	5	7/24/91	7/24/91	148	200	74	73	1.4	1.9
305	6	7/25/91	7/25/91	124*	200	62			
306	6	7/25/91	7/25/91	152	200	76	69	9.9	14

OVERALL: 72 4.9 6.7

* Low recovery due to leak during extraction.

Table 3-VII. Storage dissipation data for the Metam Sodium Study (room temperature, pH 10).

Study: X56
 Analyte: MITC
 MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Jean Hsu
 Method: GC/NPD

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
206	0	7/19/91	7/19/91	129	200	64			
207	0	7/19/91	7/19/91	120	200	60	62	3	5
215	1	7/20/91	7/20/91	93	200	47			
216	1	7/20/91	7/20/91	90	200	45	46	1.4	3.1
225	2	7/21/91	7/21/91	48	200	24			
226	2	7/21/91	7/21/91	50	200	25	25	0.71	2.9
234	3	7/22/91	7/22/91	27.6	200	14			
235	3	7/22/91	7/22/91	27.6	200	14	14	0.0	0.0
271	4	7/23/91	7/23/91	9.5	200	4.7			
272	4	7/23/91	7/23/91	9.0	200	4.5	5	0.1	3.1
280	5	7/24/91	7/24/91	8	200	4.2			
281	5	7/24/91	7/24/91	8	200	4.2	4	0.0	0.0
307	6	7/25/91	7/25/91	nd	200	0			
308	6	7/25/91	7/25/91	nd	200	0	0	0.0	0.0
OVERALL:							22	23	102

Table 3-VIII. Storage dissipation data for the Metam Sodium Study (refrigerated, pH 10).

Study: X56
 Analyte: MITC
 MDL: 5 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: CDFA
 Chemist: Jean Hsu
 Method: GC/NPD

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
208	0	7/19/91	7/19/91	133	200	67			
209	0	7/19/91	7/19/91	116	200	58	63	6.4	10
217	1	7/20/91	7/20/91	110	200	55			
218	1	7/20/91	7/20/91	114	200	57	56	1.4	2.5
227	2	7/21/91	7/21/91	106	200	53			
228	2	7/21/91	7/21/91	106	200	53	53	0.0	0.0
236	3	7/22/91	7/22/91	97	200	48			
237	3	7/22/91	7/22/91	103	200	52	50	2.8	5.7
273	4	7/23/91	7/23/91	89.7	200	45			
274	4	7/23/91	7/23/91	89.7	200	45	45	0.00	0.00
282	5	7/24/91	7/24/91	90	200	45			
283	5	7/24/91	7/24/91	93	200	47	46	1.4	3.1
309	6	7/25/91	7/25/91	83	200	41			
310	6	7/25/91	7/25/91	79	200	40	41	0.71	1.7
OVERALL:							50	7.4	15

Table 3-VIII. Continuing quality control data for the Metam Sodium Study.

Study: X56
 Analyte: MTC
 MDL: 2 ppb
 Date of Report: 8/1/91

Sample Type: Surface water
 Lab: APPL
 Chemist: Mike Ray
 Method: GC/ purge and trap/ PID/FID

Extraction Set No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	\bar{X}	SD	CV (%)
9, 28, 33, 45, 51, 57	R9265	23.1	25.0	92.4	91	1.0	1.1
		22.7	25.0	90.8			
		22.5	25.0	90.0			
		22.8	25.0	91.2			
19, 23, 39, 42, 61, 64, 135	R9285	22.1	25.0	88.4	90	2.3	2.5
		22.1	25.0	88.4			
		22.7	25.0	90.8			
		23.3	25.0	93.2			
65, 69, 73, 77, 85, 81, 93, 89, 257, 261, 265, 269, 68, 72, 76, 80, 88, 84, 96, 92, 260, 264, 268, 272	R9306	22.8	25.0	91.2	90	1.3	1.4
		22.5	25.0	90.0			
		22.1	25.0	88.4			
		22.2	25.0	88.8			
65, 69, 73, 77, 85, 81, 93, 89, 257, 261, 265, 269, 68, 72, 76, 80, 88, 84, 96, 92, 260, 264, 268, 272	R9306	9.23	10.0	92.3	94	3.4	3.6
		9.23	10.0	92.3			
		9.36	10.0	93.6			
		9.94	10.0	99.4			
4, 16, 277, 280, 273, 276	R9314	9.92	10.0	99.2	100	2.97	2.98
		9.60	10.0	96.0			
		10.26	10.0	103			
		10.09	10.0	101			
OVERALL:					93	4.4	4.7